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## In-Plane Anisotropy of Upper Critical Field in $\text{Sr}_2\text{RuO}_4$

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We investigated the behavior of the spin-triplet superconductor  $\text{Sr}_2\text{RuO}_4$  ( $T_c \approx 1.5$  K) under the magnetic fields parallel to the quasi-two-dimensional plane. The upper critical field  $H_{c2}$  exhibits a clear fourfold anisotropy of about 3% at 0.35 K. Furthermore, we detected an additional transition feature below  $H_{c2}$  in both the ac susceptibility and the specific heat. These second-transition features as well as the pronounced in-plane  $H_{c2}$  anisotropy disappear above 0.8 K or under intentional field misalignment of less than  $1^\circ$ . Most of these characteristics are consistent with the predicted emergence of the second superconducting phase with a line-node gap.

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After the discovery of superconductivity in the layered perovskite  $\text{Sr}_2\text{RuO}_4$  [1], the possibility of  $p$ -wave superconductivity was proposed on the basis of the similarity of the Fermi liquid parameters of  $\text{Sr}_2\text{RuO}_4$  to those of  $^3\text{He}$  and of the presence of the ferromagnetic relative compound [2]. Successive experiments [3], as well as theory [4], have given substantial support for this expectation. In particular, the NMR experiment has revealed that the spin susceptibility remains totally unchanged through the superconducting transition temperature  $T_c$  [5], providing a definitive identification that  $\text{Sr}_2\text{RuO}_4$  is a spin-triplet superconductor. Secondly, muon spin relaxation ( $\mu\text{SR}$ ) measurement revealed that a spontaneous internal magnetic field develops below  $T_c$  [6], strongly suggesting that the superconducting state breaks time reversal symmetry. These two experimental results lead us to infer that the  $p$ -wave superconducting state represented by the two-component  $d$  vector  $\mathbf{d} = \hat{z}(k_x + ik_y)$  with the nodeless gap  $|\Delta| = (k_x^2 + k_y^2)^{1/2}$  ( $\hat{z}$  and  $k_x + ik_y$  are the spin and orbital parts of the wave function) is the most probable one among the possibilities examined theoretically [2].

In principle, the spin-triplet  $p$ -wave state may have multiple superconducting phases because of allowed spin and orbital degrees of freedom of the Cooper pairs, as seen in heavy Fermion superconductor  $\text{UPt}_3$  [7] and analogously in superfluid  $^3\text{He}$  [8]. The  $d$ -vector consisting of a two-component order parameter allows a state with different symmetry to be stabilized near  $H_{c2}$ . For  $\text{Sr}_2\text{RuO}_4$ , this state has a line-node gap, the presence of which should enhance the in-plane  $H_{c2}$  anisotropy [9]. Therefore, investigating the characteristics of the in-plane  $H_{c2}$  anisotropy and searching for the second transition from the nodeless to line-node gap state may be of decisive importance in confirming the superconducting order parameter of  $\text{Sr}_2\text{RuO}_4$ .

In this Letter, we report on the precise measurements of the angular dependence of the in-plane  $H_{c2}$  of  $\text{Sr}_2\text{RuO}_4$ . We indeed observed the in-plane  $H_{c2}$  anisotropy with fourfold symmetry, and it is noticeably enhanced below 0.8 K. In addition, we detected a feature which is attributable to

the second transition at temperatures below 0.8 K in both ac susceptibility and specific heat measurements for fields parallel to the  $ab$  plane.

The single crystals of  $\text{Sr}_2\text{RuO}_4$  used in this study were grown by a floating-zone method with an infrared image furnace. We measured angular dependence of the in-plane  $H_{c2}$  for two samples (denoted by A and B below) and specific heat under magnetic fields for one sample (C). Samples A (dimension  $2.2 \times 2.0 \times 1.3 \text{ mm}^3$ ) and C ( $2.8 \times 4.8 \times 0.5 \text{ mm}^3$ ) are as-grown crystals, and sample B ( $1.9 \times 1.3 \times 0.5 \text{ mm}^3$ ) was annealed in oxygen at  $1050^\circ\text{C}$  for three weeks. For all three samples, the shortest dimension was parallel to  $[001]$ . The x-ray rocking curves of these samples all showed single crystal characters with the diffraction peak width [full width of half maximum (FWHM)  $\approx 0.08^\circ$ ] comparable to that of Si crystal ( $0.06^\circ$ ) in our diffractometer. The direction of the tetragonal crystallographic axes for these three samples was determined by x-ray Laue pictures. The side surface of sample A was aligned along the basal  $[100]$  axis by diamond polishing, whereas those of samples B and C were rotated from the  $[100]$  axis by about  $25^\circ$  and  $55^\circ$ , respectively. ac susceptibility measurements indicated a sharp superconducting transition with the midpoint at  $T_c = 1.414$  K for sample A, 1.459 K for sample B, and 1.492 K for sample C.

The angular dependence of the in-plane  $H_{c2}$  was determined by ac susceptibility using a dilution refrigerator (Oxford Instruments, model Kelvinox TLM) for sample A and a  $^3\text{He}$  refrigerator for sample B. Both refrigerators are equipped with double-axis rotators. The ac susceptibility was measured by a mutual-inductance method with an ac field of 0.05 mT at a frequency of 700 Hz for sample A and 1.6 kHz for sample B. The ac field was maintained parallel to the  $[001]$  direction, thus perpendicular to the dc field ( $H_{dc}$ ) for  $H_{dc} //$  the  $ab$  plane. The specific-heat measurements under magnetic fields for sample C were conducted by a relaxation method using another dilution refrigerator equipped with a single-axis rotator. Details of

the specific-heat experiments will be published elsewhere [10]. Below, we will mainly focus on the ac susceptibility measurements.

To specify the direction of the field with respect to the crystalline axes, we adopt the polar angle  $\theta$ , for which  $\theta = 0^\circ$  is along the  $[001]$  direction, and the azimuthal angle  $\phi$ , for which  $\phi = 0^\circ$  with  $\theta = 90^\circ$  is along the  $[100]$  direction. The  $ab$  plane of the sample was aligned exactly parallel to  $H_{dc}$  by changing  $\theta$  for each  $\phi$  while observing the change in the ac susceptibility; the alignment was repeated whenever  $\phi$  was changed. The accuracy of the exact parallel alignment for our experiment was as high as  $0.02^\circ$ . The in-plane  $H_{c2}$  measured using the present method with the accuracy of  $\Delta\theta = -0.00 \sim +0.02^\circ$  guarantees the precision in  $\delta H_{c2}/H_{c2}$  of better than 0.1% at low temperatures.

Figure 1 shows the angular dependence of in-plane  $H_{c2}$  of both samples A (closed circles) and B (open diamonds) measured at  $T = 0.10$  and  $0.35$  K, respectively. Here we define  $H_{c2}$  as the intersection of the linear extrapolation of the most rapidly changing part of  $\chi'$  (the in-phase component of ac susceptibility) and that of normal state  $\chi'$  [Fig. 2(a)]. Both samples clearly show a fourfold anisotropy. The maximum in  $H_{c2}$  appears in the diagonal directions ( $[110]$  and  $[-110]$ ), and the minimum in  $H_{c2}$  in the principal basal directions ( $[100]$  and  $[010]$ ), corresponding to the Ru-O bonding directions. The magnitude of the anisotropy is  $\Delta H_{c2}/H_{c2}(110) = 0.026$  [ $\Delta H_{c2}$  is defined as  $H_{c2}(110) - H_{c2}(010)$ ] for sample A at  $0.10$  K and  $0.028$  for sample B at  $0.35$  K. Here it is worth noting that although the crystallographic axes of samples A and B have different orientation with respect to the physical surfaces as described above, they exhibit the same symmetry in the in-plane  $H_{c2}$  anisotropy. This fact excludes the possibility that the in-plane  $H_{c2}$  anisotropy shown in Fig. 1 is caused by surface superconductivity as observed in  $UPT_3$  [11].

The inset in Fig. 1 shows the variation of the absolute magnitude of the in-plane  $H_{c2}$  anisotropy with temperature for sample B. Each data point was taken by sweeping the field at constant temperature. A rapid increase in  $\Delta H_{c2}$  occurs below  $0.8$  K. The variation is much more gradual for  $T > 0.8$  K, and  $\Delta H_{c2}$  tends to be negative for  $T > 1.15$  K before it approaches zero at  $T_c$ .

Anisotropic  $H_{c2}$  was observed previously in cubic materials such as clean Nb, V [12], and  $V_3Si$  [13], and recently in borocarbides such as  $LuNi_2B_2C$  [14] and in high- $T_c$  cuprates [15]. In these materials the in-plane  $H_{c2}$  anisotropy arises from the anisotropy of the Fermi surface (FS) and/or of the superconducting pairing interaction. The absolute magnitude of the anisotropy due to these effects generally shows a monotonic decrease with increasing temperature, unless superconductivity competes with magnetic ordering, for example, in  $TmNi_2B_2C$  [16]. This is in contrast with the present observation in  $Sr_2RuO_4$ , and in particular, the enhanced  $H_{c2}$  anisotropy below  $0.8$  K as shown in the inset of Fig. 1 is suggestive of a different origin.

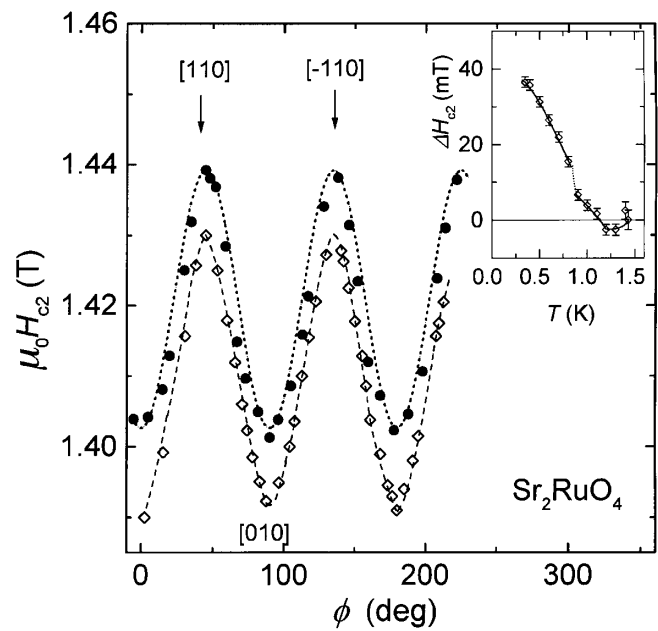


FIG. 1. The angular dependence of the in-plane  $H_{c2}$ . Closed circles: data of sample A measured at  $0.10$  K; open diamonds: sample B at  $0.35$  K. The crystallographic axes of samples A and B have different orientations with respect to the physical surfaces (see text). The inset shows the variation of the in-plane  $H_{c2}$  anisotropy with temperature for sample B,  $\Delta H_{c2} = H_{c2}(110) - H_{c2}(010)$ . The curves are guides to the eye.

Next, let us make further discussion on the possibility of the  $H_{c2}$  anisotropy induced by the line-node state. For the two-component  $d$  vector, the line-node state near  $H_{c2}$  is expected because the presence of line nodes can considerably decrease the kinetic energy generated by superconducting screening current, and hence the orbital depairing effect. It is naturally deduced that the line

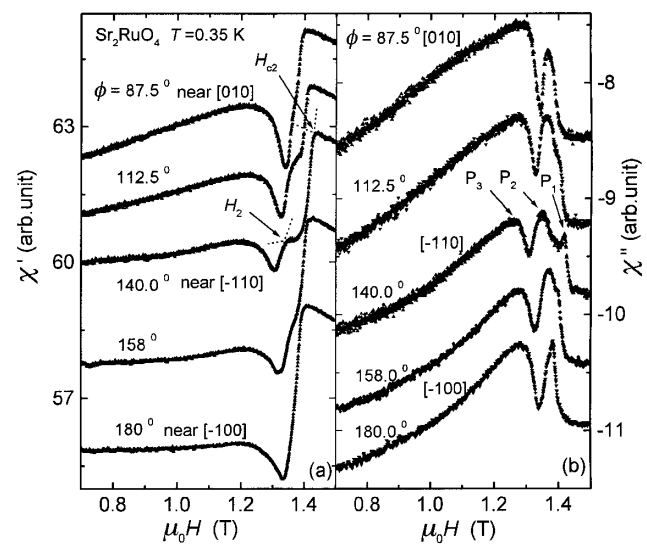


FIG. 2. ac susceptibility as a function of  $H_{dc}$  measured at different angles of  $\phi$  for sample B. (a)  $\chi'$ ; (b)  $\chi''$ . Features  $P_1$ ,  $P_2$ , and  $P_3$  are described in the text.  $H_2$ : The transition field corresponding to  $P_2$ .

nodes should appear in the in-plane direction perpendicular to the field and run along  $k_z$ . From the theoretical considerations for the allowed symmetries of the pairing states [9,17], this line-node state is expressed by  $d = \hat{z}k_{x'}$  with the gap  $|\Delta| = |k_{x'}|$ , where  $x'$  is always along the external field direction, and hence rotates with the field. We anticipate the in-plane  $H_{c2}$  anisotropy to be enhanced in the line-node state, provided that the density of state at FS is anisotropic. Agterberg [9] calculated such in-plane  $H_{c2}$  anisotropy using Ginzberg-Landau (GL) theory with a two-component superconducting order parameter. Our experimental observation on the in-plane  $H_{c2}$  anisotropy is in qualitative agreement with this theoretical prediction.

If the line-node state near  $H_{c2}$  does appear, we naturally expect a second superconducting transition with decreasing field, because the fully gapped state which is most probably stable at lower fields has a different symmetry. We should emphasize here that the clear transition can occur only if the field is applied *exactly* parallel to the  $ab$  plane; otherwise the line-node formation is incomplete and only crossover behavior is expected. Let us next examine whether our ac susceptibility data display any feature reflecting the possible second superconducting transition. Figures 2(a) and 2(b) represent  $\chi'$  and  $\chi''$  (the out-of-phase, dissipation component) as a function of dc field exactly parallel to the  $ab$  plane at some typical positions of  $\phi$  for sample B. We can clearly see that both  $\chi'$  and  $\chi''$  show distinct anisotropy with  $\phi$ . When the field orients nearly along [010] [the top curves in Fig. 2(b)], the main dissipation peak corresponding to the superconducting transition is a single peak. With increasing  $\phi$ , a shoulder peak gradually develops, and the main peak splits into two peaks ( $P_1$  and  $P_2$ ) for  $H_{dc}$  along the diagonal direction ([−110]). From [−110] to [−100], these two peaks merge into a single peak again. Apart from these two peaks, one other peak ( $P_3$ ) was also observed. Yoshida *et al.* [18] has studied this peak and attributed it to the vortex synchronization pinning. Then the feature  $P_2$  most probably corresponds to the expected transition. The presence of these three peaks in  $\chi''$  and their evolution with respect to the field orientation are reproducible in sample A.

Additionally, we checked the effect of intentional misalignment on the additional peak  $P_2$  for sample B. We found that the misalignment of  $\Delta\theta \sim 0.6^\circ$  fully suppresses the satellite peak  $P_2$  (not shown here). In contrast, the misalignment has only a minor influence on the “conventional” vortex peak  $P_3$  as expected. It should be noted that the field misalignment has a strong effect also on the magnitude of the in-plane  $H_{c2}$  anisotropy.  $\Delta H_{c2}/H_{c2}$  decreases from 0.028 with  $\Delta\theta \leq 0.02^\circ$  to 0.007 with  $\Delta\theta = 0.60^\circ$  and to a slightly negative value of  $-0.002$  with  $\Delta\theta = 1.20^\circ$ .

The temperature dependence of the transition field  $H_2$  [see Fig. 2(a) for definition], corresponding to the additional feature  $P_2$ , in the direction of  $H_{dc} // [110]$  for sample B is shown in the phase diagram of Fig. 3. The

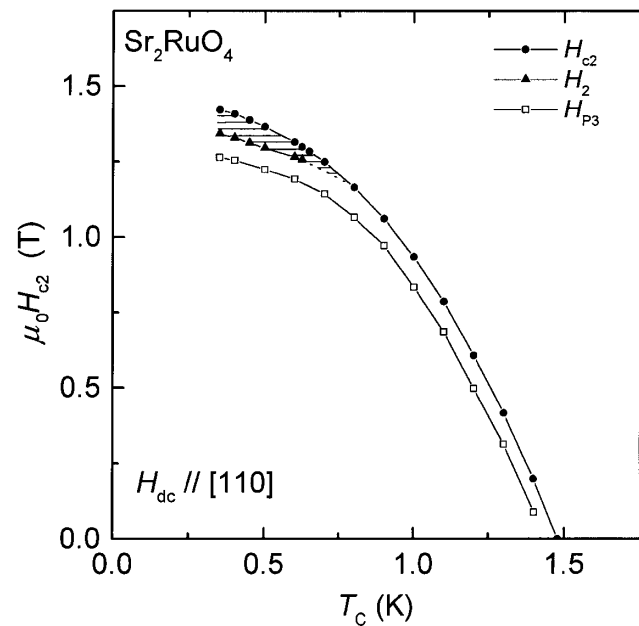


FIG. 3. The phase diagram for  $H_{dc} // [110]$ .  $H_2$ : the transition field corresponding to  $P_2$  [its definition is shown in Fig. 2(a)].  $H_{P3}$ : the peak position of  $P_3$  in  $\chi''$ .

temperature dependence of  $P_3$  (peak position) is also plotted in Fig. 3. It shows that the feature  $P_2$  becomes undetectable at  $T > 0.7$  K. The extrapolation of the curve for  $H_2$  merges with that for  $H_{c2}$  at about 0.8 K. Experimentally, there is remarkable correlation between the feature  $P_2$  and the pronounced in-plane  $H_{c2}$  anisotropy below 0.8 K (see the inset of Fig. 1), because both are simultaneously suppressed above 0.8 K or under slight field misalignment of less than  $1^\circ$ .

To further characterize this additional transition feature, we performed specific heat measurements for sample C under fields parallel to [110] as shown in the main panel of Fig. 4. The accuracy of the field alignment was  $\Delta\phi \approx 3^\circ$  and  $\Delta\theta \approx 0.3^\circ$ . The temperature dependence of  $C_e/T$  ( $C_e$ : electronic contribution of the specific heat) with  $H > 1.2$  T shows an anomalous behavior compared with the data for  $H < 1.2$  T. The variation of  $C_e/T$  with  $T$  is nearly  $T$ -linear at low temperatures and shows a conventional downward concave character as temperature approaches  $T_c(H)$  for  $H < 1.2$  T, while for  $H > 1.2$  T the  $C_e/T$  shows a sharp additional increase somewhat below  $T_c(H)$ . We also found that misalignment of less than  $1^\circ$  can fully suppress this anomalous behavior, as shown in the inset of Fig. 4. Obviously this unusual behavior in  $C_e/T$  with  $H > 1.2$  T can be ascribed to the substantial entropy release from the additional transition, which is revealed by ac susceptibility measurements (it occurs only with  $H > 1.2$  T; see Fig. 3). The relative amount of the entropy release induced by the additional transition at 1.4 T is  $\approx 9\%$  of the total entropy release associated with the superconducting transition. This fact confirms that the additional transition is a thermodynamic transition, not merely a vortex-lattice transition. The reason why we did not see



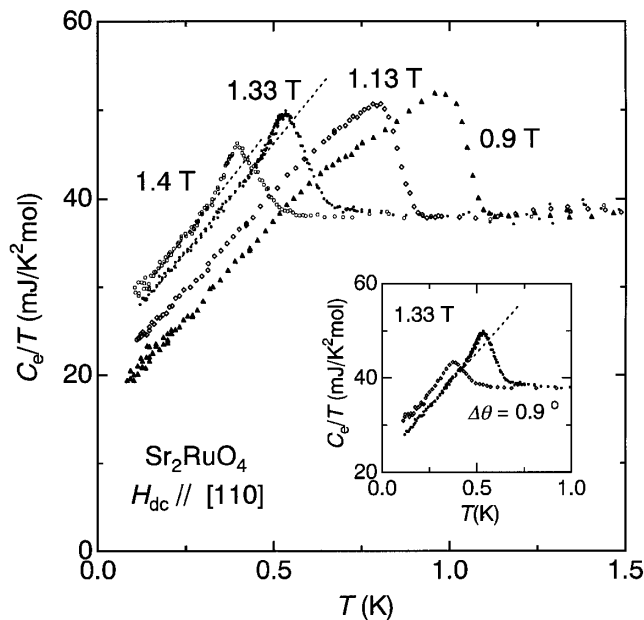


FIG. 4. Temperature dependence of the specific heat divided by temperature of sample C with magnetic fields parallel to [110]. The inset shows the effect of an intentional slight field misalignment. The dotted lines are guides to the eye.

a clear splitting in specific heat jump may be due to the larger uncertainty in the field alignment.

Combining the results of specific heat and ac susceptibility, it is natural to interpret the peak  $P_2$  as being due to the second superconducting transition. To our knowledge, the only plausible explanation available for the second superconducting transition in  $\text{Sr}_2\text{RuO}_4$  is due to the emergence of the line-node state [9]. In this case, the corresponding enhancement of the in-plane  $H_{c2}$  anisotropy is also naturally understood. Moreover, the point in the phase diagram where  $H_{c2}$  and the extrapolation of  $H_2$  intersect may be regarded as the bicritical point.

Finally, we should point out that although the fourfold symmetry of the in-plane  $H_{c2}$  anisotropy observed experimentally is in qualitative agreement with the theoretical expectation by Agterberg [9], the temperature dependence of both the  $H_{c2}$  anisotropy and the second transition predicted by this theory is different from our experimental observations. In that theory, the second transition as well as the associated in-plane  $H_{c2}$  anisotropy should persist up to  $T_c(H = 0)$ . In comparison, our experiments show that the second transition feature appears only at low temperatures and that the in-plane  $H_{c2}$  anisotropy sharply reduced above 0.8 K. The reason for this discrepancy is not known at present.

In summary, we have observed the fourfold anisotropy of in-plane  $H_{c2}$  of  $\text{Sr}_2\text{RuO}_4$ , the magnitude of which shows a sharp decrease above 0.8 K or under slight field misalign-

ment. We also observed the feature which is attributable to the second superconducting transition only in the  $H$ - $T$  region where the in-plane  $H_{c2}$  anisotropy is enhanced. All of these results are consistent with the emergence of a new superconducting state with a line-node gap at  $T < 0.8$  K in the field exactly parallel to the  $ab$  plane.

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